

LA-UR-19-20639

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Intended for: LDRD program review

Issued: 2019-01-28

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AnO₂-Cl Coordination Chemistry at High P/T

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Jason Baker, Artas Migdisssov, Hakim Boukhalfa, Hongwu Xu**

20180007DR Project Appraisal

January 31, 2019



Technical Goals

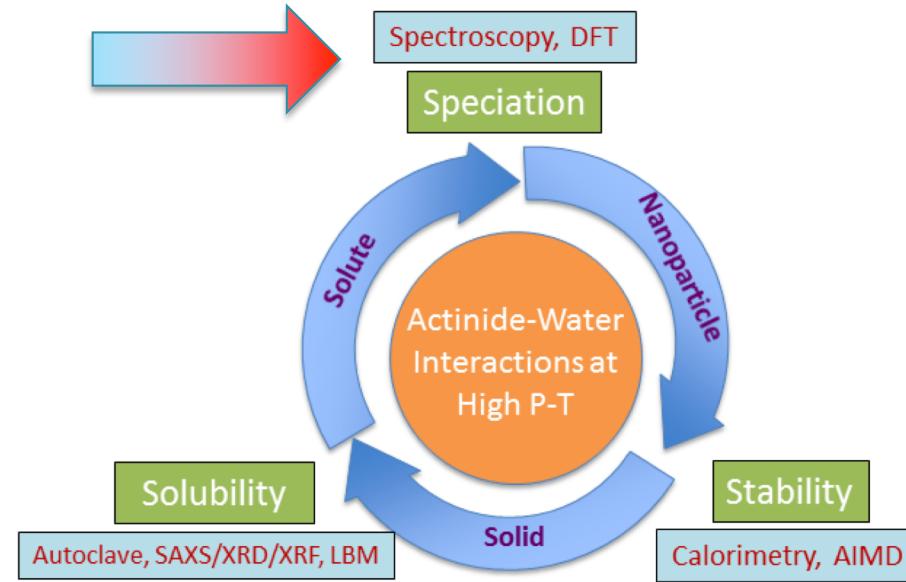
Four tasks:

- » Materials synthesis & characterization
- » In-situ structural determination using synchrotron and Raman techniques
- » Thermodynamic measurements (solubility measurements + calorimetry)
- » **Multiscale modeling**

Speciation/Solubility/Stability (three thrust areas):

microscopic structure — macroscopic thermodynamics

Structure -Stability Relationship



Outline: AnO₂²⁺-Cl

- » AnO₂²⁺: An=U, Pu
- » Speciation
- » Stability -- their thermodynamics
- » P-T impact on speciation and stability
- » Spectroscopy: IR and UV-vis

The diagram illustrates the relationship between Complexity and Radioactivity for various actinide species. A horizontal blue arrow labeled "Complexity" points from left to right, with two red arrows pointing downwards from it to the table rows. A vertical red arrow labeled "Radioactivity" points downwards from the top of the table to the first row.

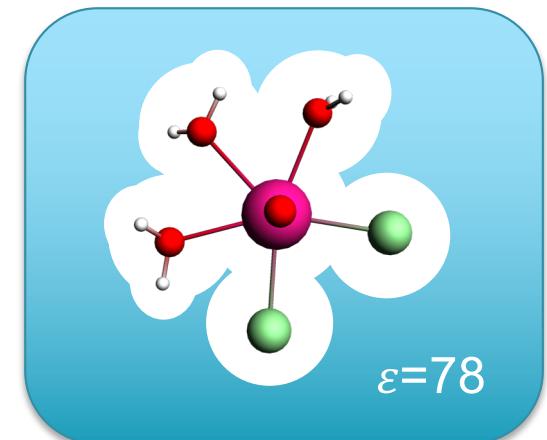
	Aqueous solution	Simple oxide	Non-oxide	Ternary system
U	U(Cl ⁻), U(CO ₃ ²⁻), U(SO ₄ ²⁻ for U(IV) & U(VI))	UO ₂ , U ₄ O ₉ , U ₃ O ₇ , U ₃ O ₈ , UO ₃ polymorphs	USi, U ₃ Si ₂ , U ₃ Si ₅ , U ₃ Si, UN	USiO ₄ , Ca(Zr,U)Ti ₂ O ₇ , (UO ₂) ₈ O ₂ (OH) ₁₂ ·12(H ₂ O)
Th	Th ⁴⁺ /Cl ⁻ , Th ⁴⁺ /CO ₃ ²⁻ , Th ⁴⁺ /SO ₄ ²⁻	ThO ₂ , UO ₂ –ThO ₂ solid solutions	ThN	ThSiO ₄ , USiO ₄ -ThSiO ₄
Np	Np(Cl ⁻) & Np(CO ₃ ²⁻ for Np(IV), Np(V) & Np(VI))	NpO ₂ , Np ₂ O ₅	NpN	Ca(Zr,Np)Ti ₂ O ₇
Pu	Pu(Cl ⁻) & Pu(CO ₃ ²⁻ for Pu(IV), Pu(V) & Pu(VI))	PuO ₂ , UO ₂ –PuO ₂ solid solutions	PuN	Ca(Zr,Pu)Ti ₂ O ₇

Theoretical Methodology

- » **Density Functional Theory**

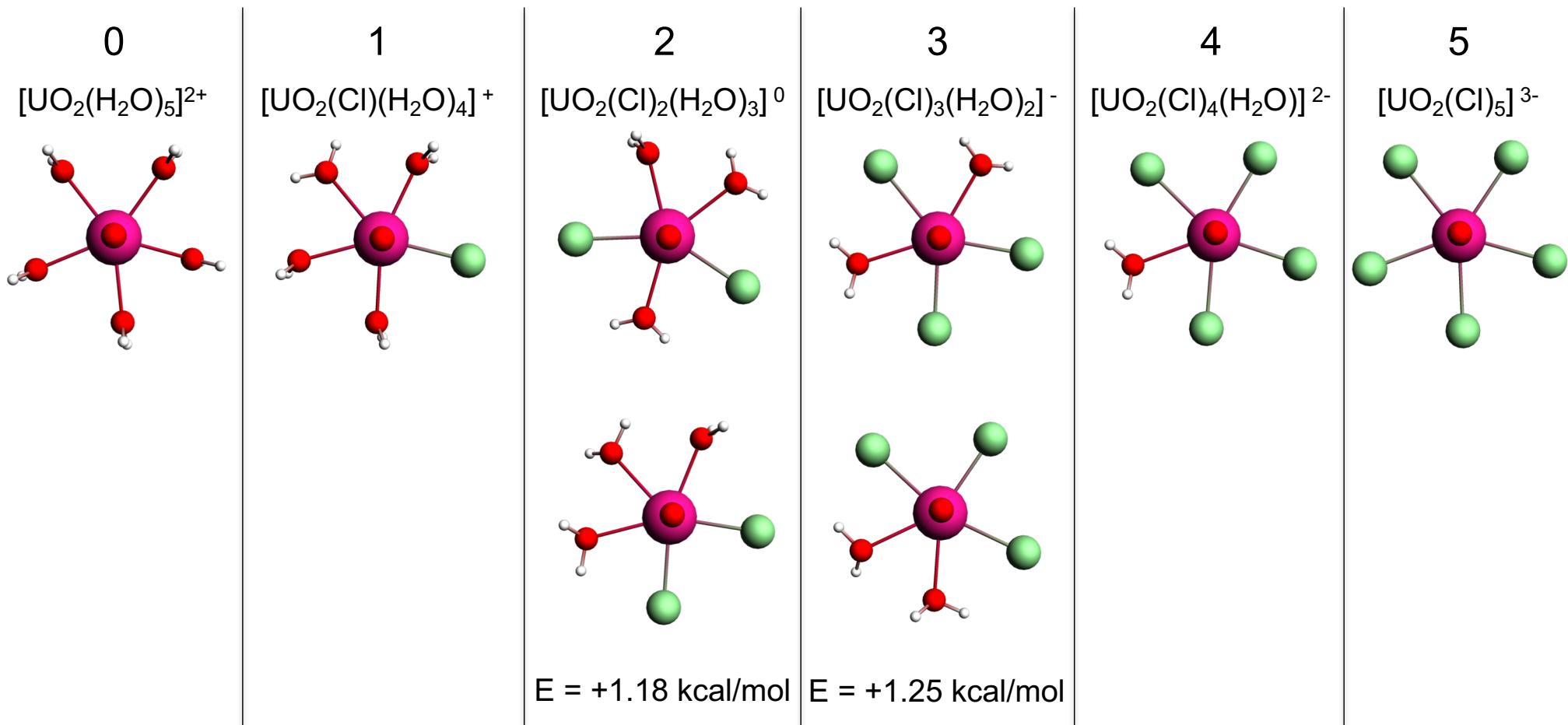
$$\left[\text{KE} + \mathbf{V}_{\text{N-e}}^{\text{Coul.}} + \int \frac{\rho_{\text{val}}}{|\vec{r} - \vec{r}'|} d^3 r' + \mathbf{V}_{\text{xc}}[\rho] + V_{\text{RECP}} \right] \psi_i = \epsilon_i \psi_i \quad \rho(r) = \sum_{i=1}^{N_v} |\psi_i(r)|^2$$

- » Hellman-Feynman forces minimization give molecular structure
- » Second derivatives of total energy yields vibrational modes and frequencies
- » Free energy: $dG = dU + p dV - T dS$
- » Entropic effects obtained via a harmonic approximation partition function
- » Solvent effects: 1st shell explicitly computed, reaction field beyond that shell



Structures: $[\text{UO}_2(\text{Cl})_n(\text{H}_2\text{O})_{5-n}]^{2-n}$

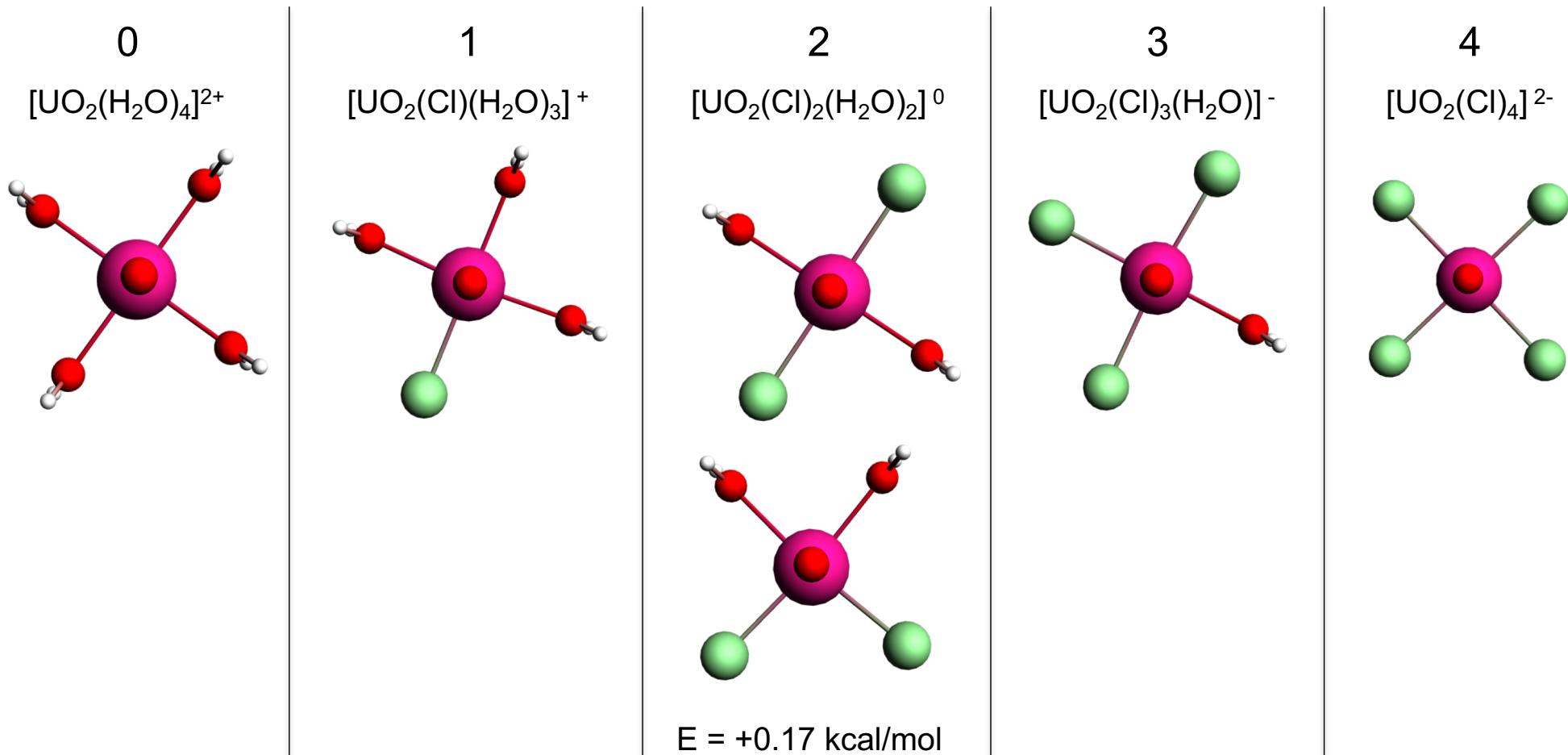
Structures as function of number of chlorine atoms coordinated:



For 5-coordination environment, stable structures identified for 0 to 5 chlorine atoms
 Structures not necessarily thermodynamically stable.

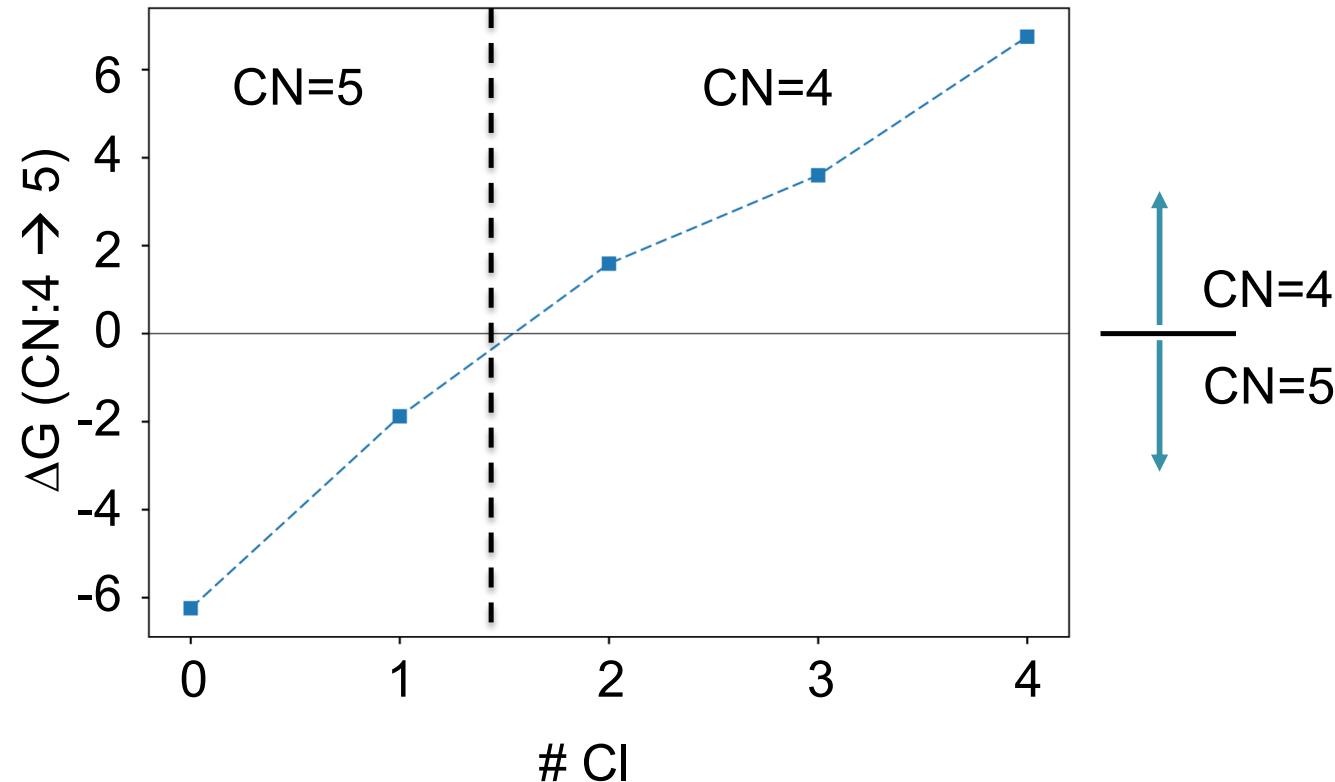
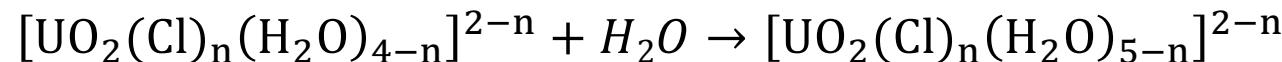
Structures: $[\text{UO}_2(\text{Cl})_n(\text{H}_2\text{O})_{4-n}]^{2-n}$

Structures as function of number of chlorine atoms coordinated:



For 4-coordination environment, stable structures identified for 0 to 4 chlorine atoms
 Structures not necessarily thermodynamically stable.

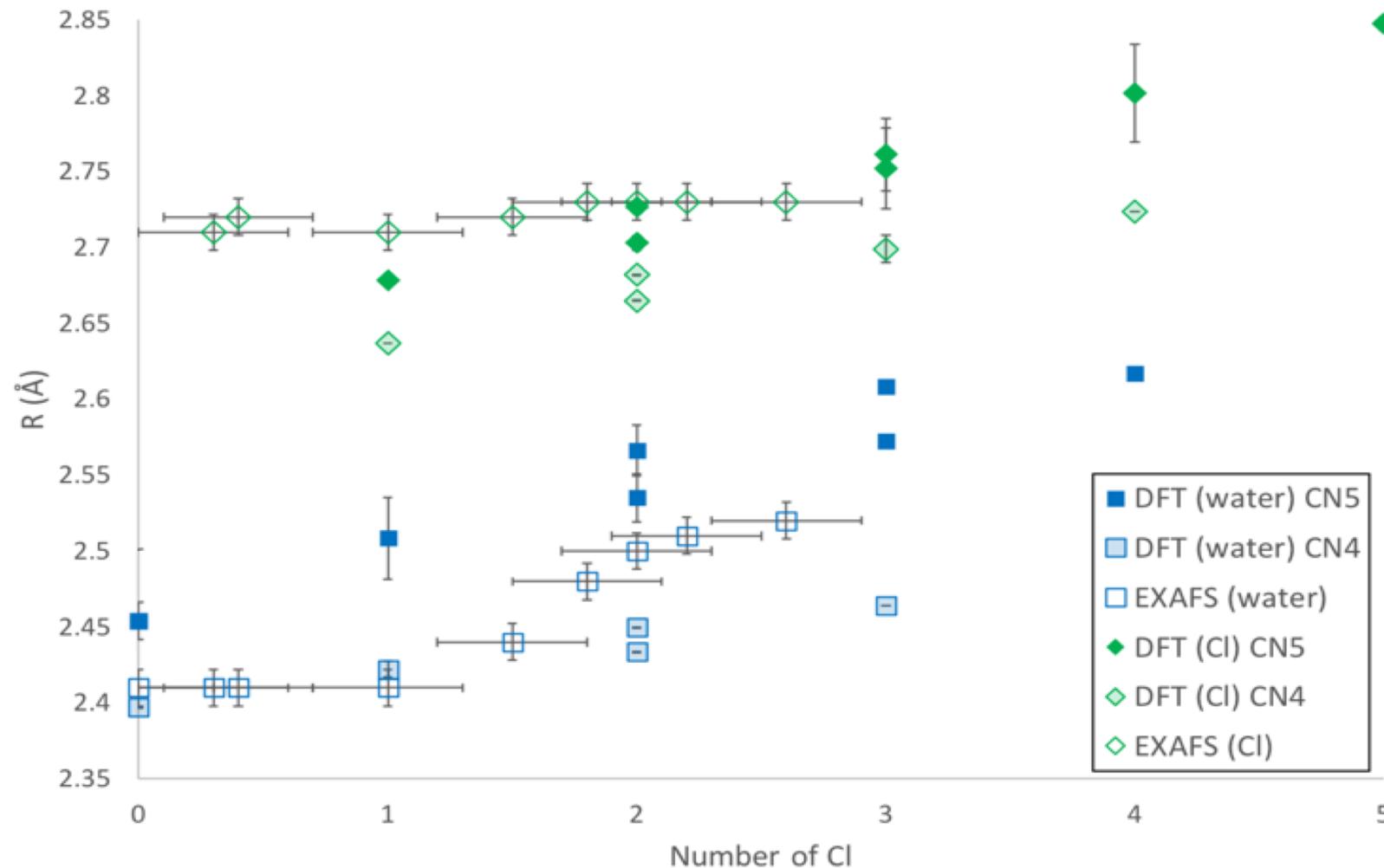
Free energy for water addition



For:

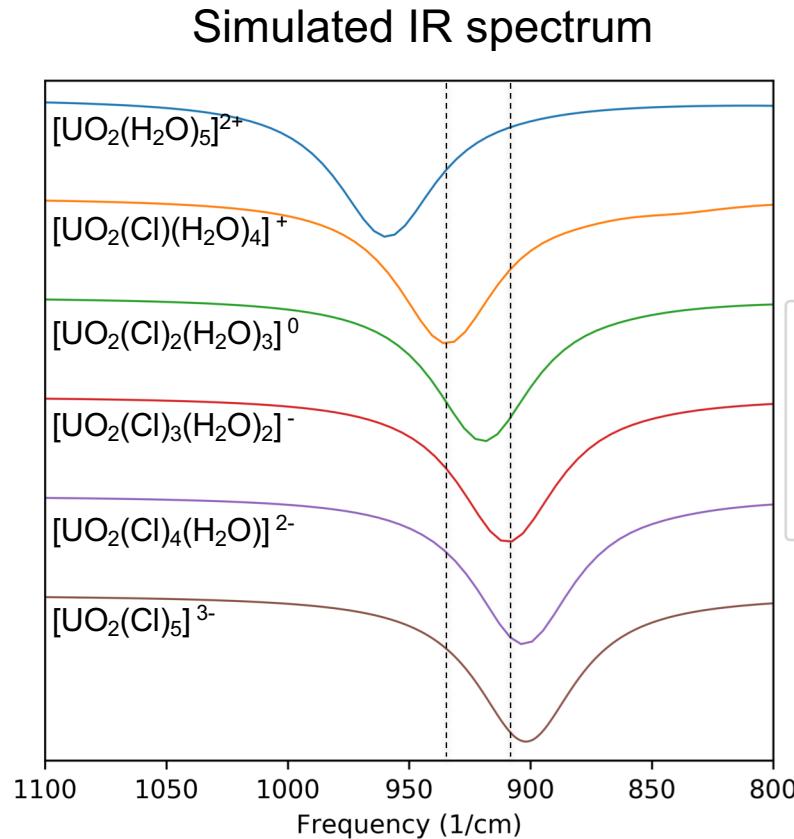
- 0 and 1 Cl atoms, CN=5 thermodynamically favorable
- 2 or more Cl, CN=4 preferred

Structural data: comparison with Experiment

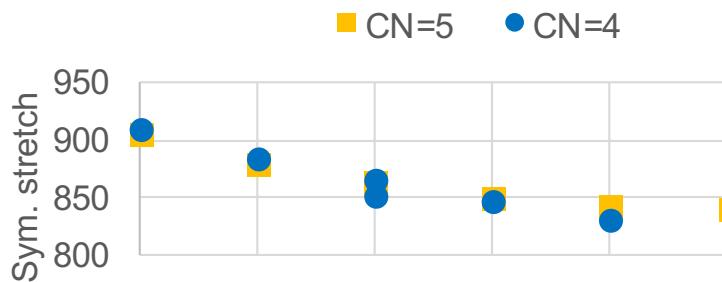


Computed structures in agreement with EXAFS measurements
for various number of Cl coordinated atoms

O=U=O vibrational frequencies

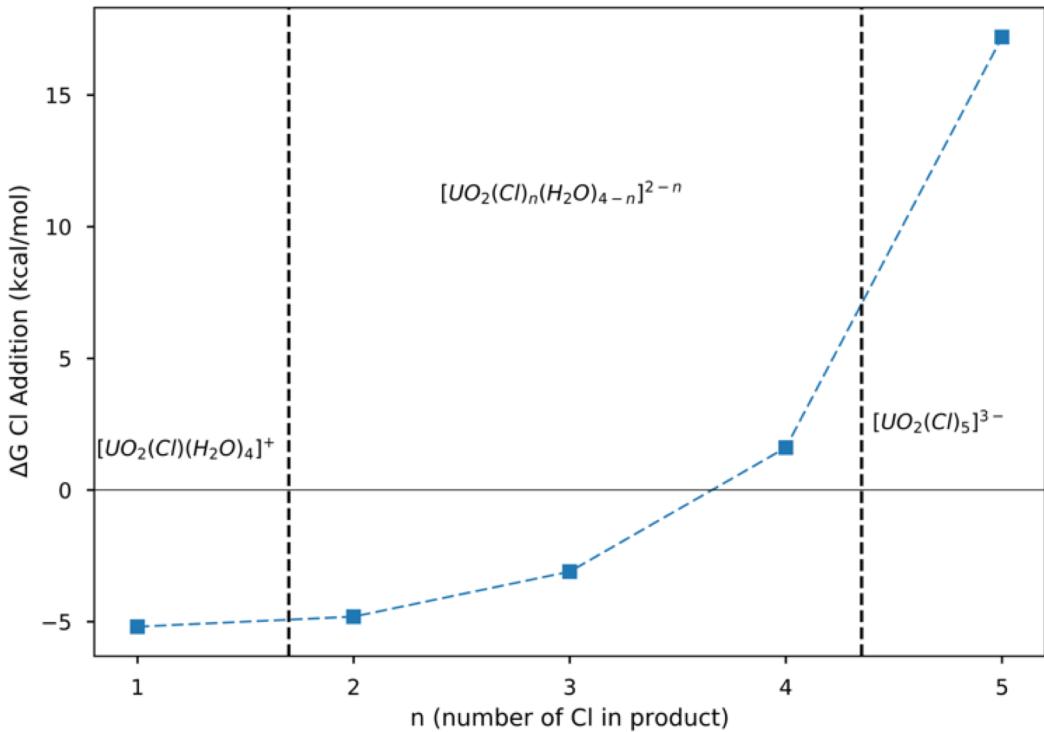


System	Sym. (cm⁻¹)	Asym. (cm⁻¹)	$\Delta\nu$
$[\text{UO}_2(\text{H}_2\text{O})_5]^{2+}$	905	959	54
$[\text{UO}_2(\text{Cl})(\text{H}_2\text{O})_4]^+$	881	934	53
$[\text{UO}_2(\text{Cl})_2(\text{H}_2\text{O})_3]^0$	863	919	56
$[\text{UO}_2(\text{Cl})_3(\text{H}_2\text{O})_2]^-$	851	909	58
$[\text{UO}_2(\text{Cl})_4(\text{H}_2\text{O})]^{2-}$	843	903	60
$[\text{UO}_2(\text{Cl})_5]^{3-}$	840	902	62
$[\text{UO}_2(\text{H}_2\text{O})_4]^{2+}$	911	961	50
$[\text{UO}_2(\text{Cl})(\text{H}_2\text{O})_3]^+$	885	942	57
$[\text{UO}_2(\text{Cl})_2(\text{H}_2\text{O})_2]^0$	866	922	56
$[\text{UO}_2(\text{Cl})_3(\text{H}_2\text{O})]^-$	847	906	59
$[\text{UO}_2(\text{Cl})_4]^{2-}$	832	890	58



- Computed Symmetric Stretch shift of 50cm⁻¹ to higher energy from UO_2Cl to UO_2Cl_3 species
- This agrees with Raman measurements at Bob's group
- Calculation supports assumption by experimentalists

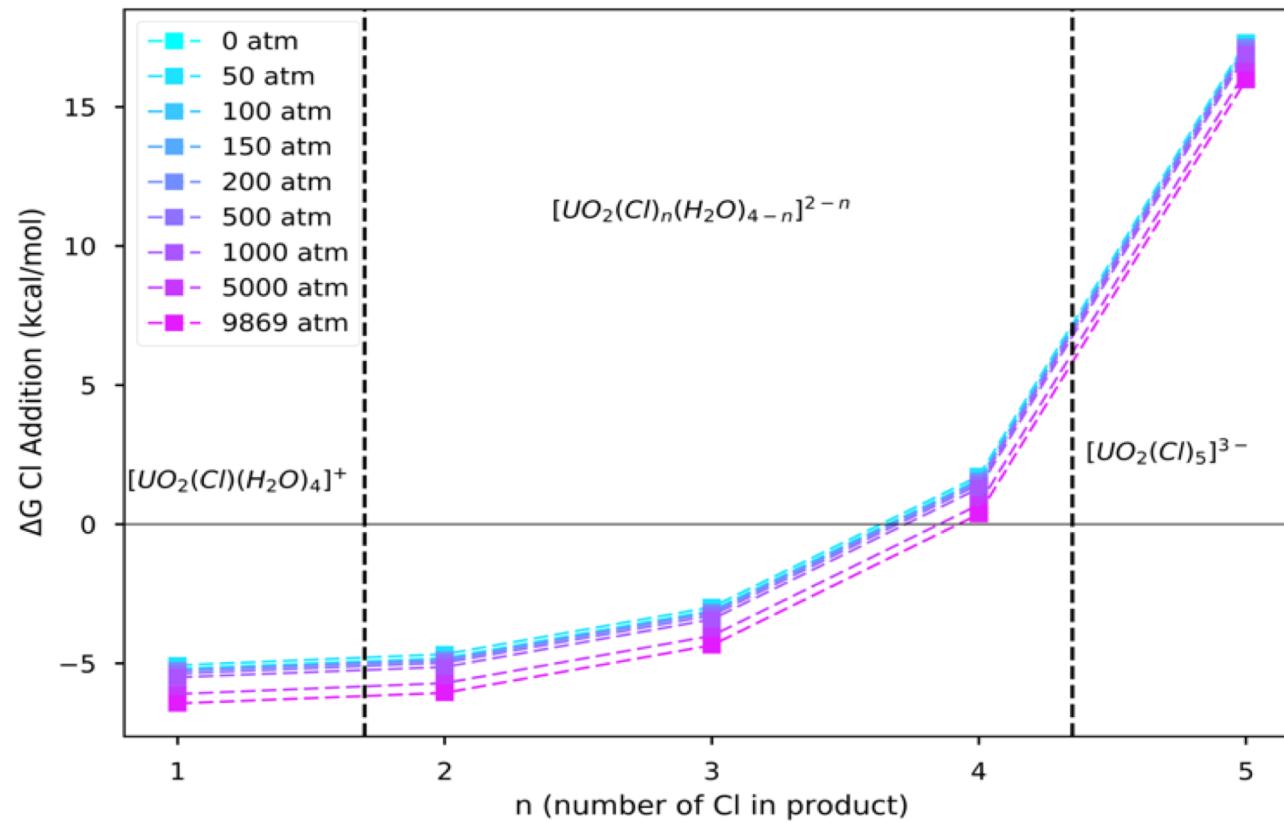
Free energy for Cl⁻ Addition



n	Reaction
1	$\text{UO}_2(\text{H}_2\text{O})_5^{2+} + \text{Cl}^- \rightarrow \text{UO}_2(\text{Cl})(\text{H}_2\text{O})_4^+ + \text{H}_2\text{O}$
2	$\text{UO}_2(\text{Cl})(\text{H}_2\text{O})_4^+ + \text{Cl}^- \rightarrow \text{UO}_2(\text{Cl})_2(\text{H}_2\text{O})_2 + 2 \text{H}_2\text{O}$
3	$\text{UO}_2(\text{Cl})_2(\text{H}_2\text{O})_2 + \text{Cl}^- \rightarrow \text{UO}_2(\text{Cl})_3(\text{H}_2\text{O})^- + \text{H}_2\text{O}$
4	$\text{UO}_2(\text{Cl})_3(\text{H}_2\text{O})^- + \text{Cl}^- \rightarrow \text{UO}_2(\text{Cl})_4^{2-} + \text{H}_2\text{O}$
5	$\text{UO}_2(\text{Cl})_4^{2-} + \text{Cl}^- \rightarrow \text{UO}_2(\text{Cl})_5^{3-}$

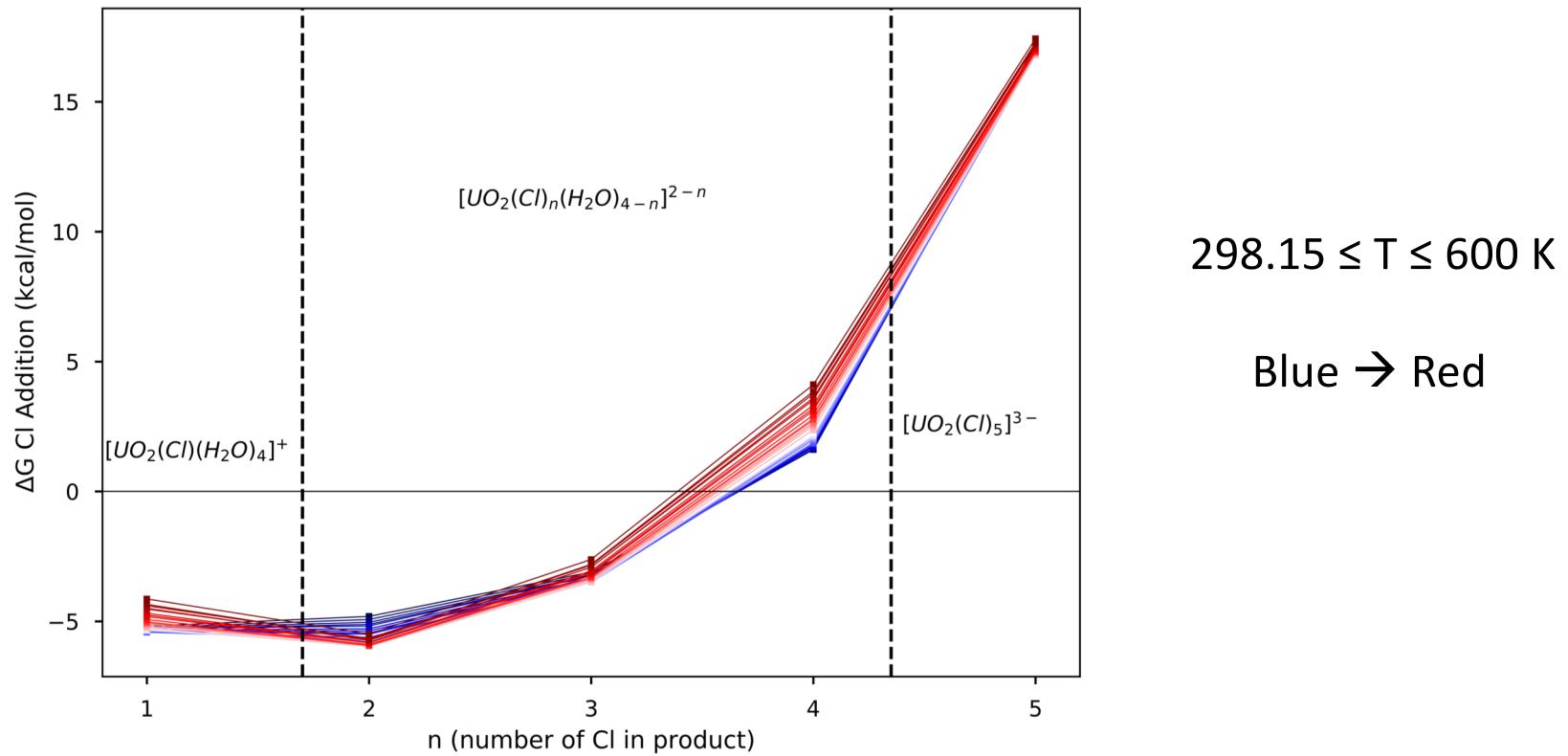
- Thermodynamically favorable additions up to 3 Cl⁻
- Relative equilibrium dependent on concentration of Cl⁻ in solution and solution activity.

Pressure effects on Cl addition



- Pressure increases ability for Cl uptake
- Effect in dG on the order of 1 kcal/mol for pressures up to 1 GPa

Temperature effects on Cl⁻ addition free energy



- Temperature-induced entropic effects opposite to pressure effects
- 4-Cl further destabilized with temperature
- Species present in solution expected to be the 0 to 3 Cl

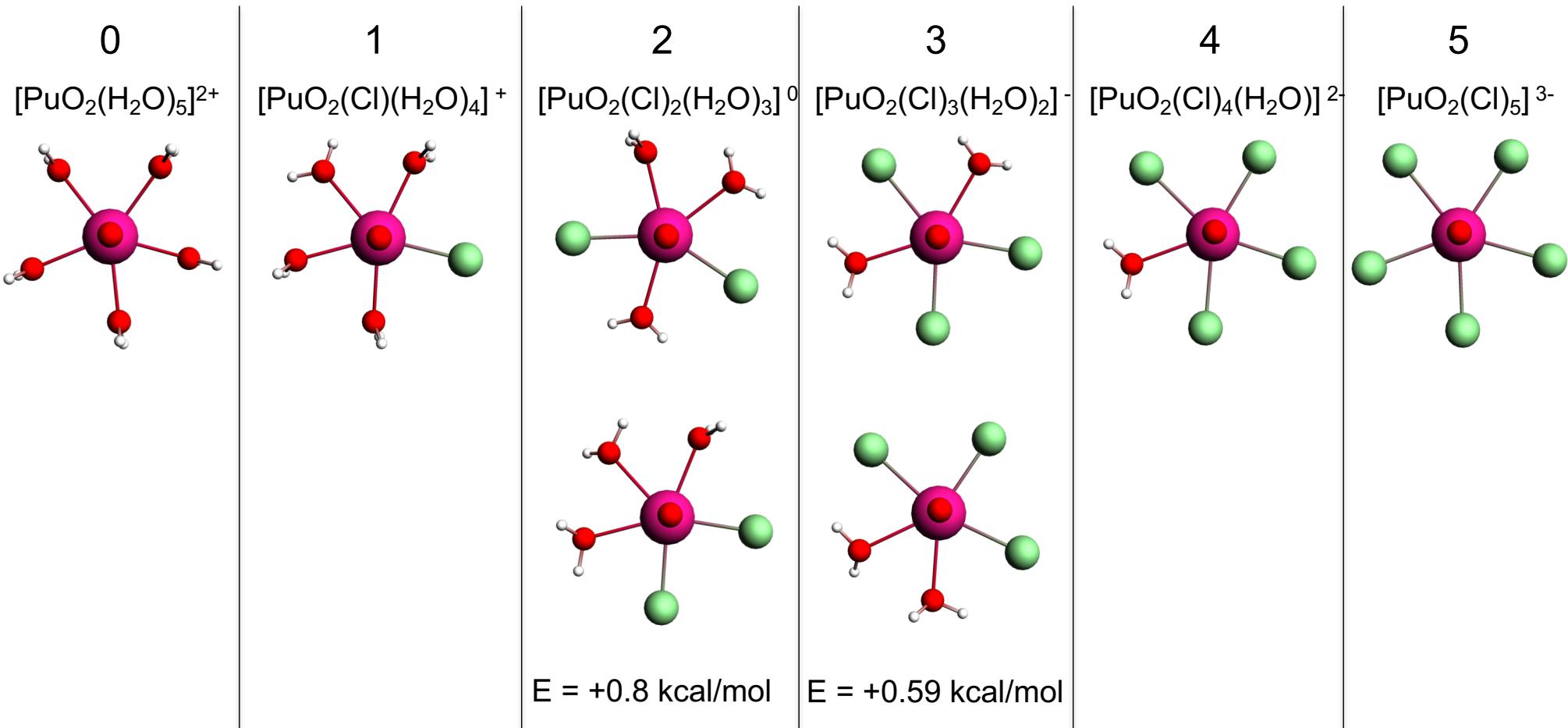
Summary of UO₂ coordination study.

- » **Predicted coordination structural parameters in agreement with previous measurements**
- » **Predicted coordination species for UO₂-Cl support 3-species picture for experimental spectra**
- » **Predicted infrared spectra yields assignments in experimental measurements.**
- » **In the range of T (298—600K) and P (1—10000 bar) the species are predicted to not change but their relative populations can be affected.**

PuO_2^{2+} :

Structures: $[\text{PuO}_2(\text{Cl})_n(\text{H}_2\text{O})_{5-n}]^{2-n}$

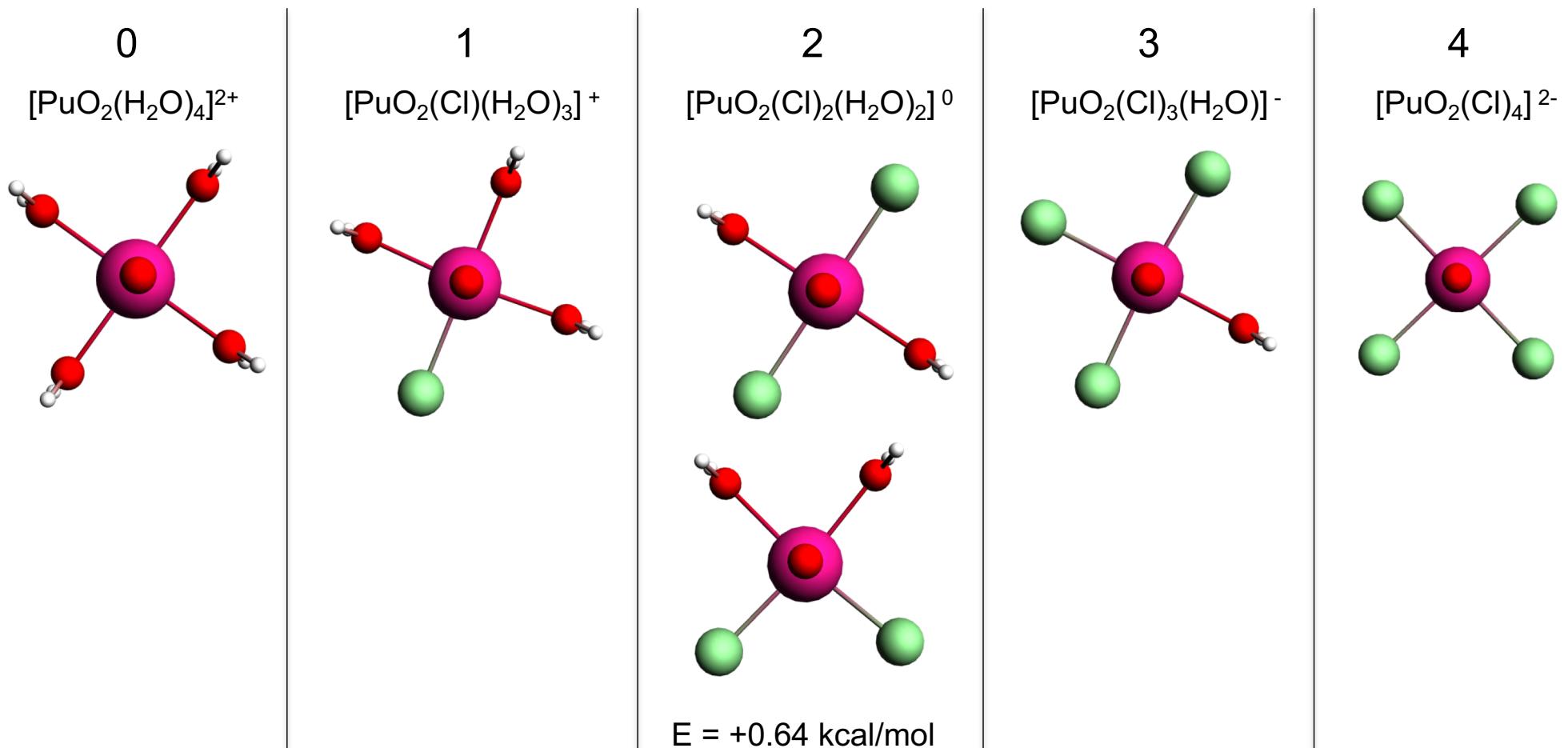
Structures as function of number of chlorine atoms coordinated:



For 5-coordination environment, stable structures identified for 0 to 5 chlorine atoms
 Structures not necessarily thermodynamically stable.

Structures: $[\text{PuO}_2(\text{Cl})_n(\text{H}_2\text{O})_{4-n}]^{2-n}$

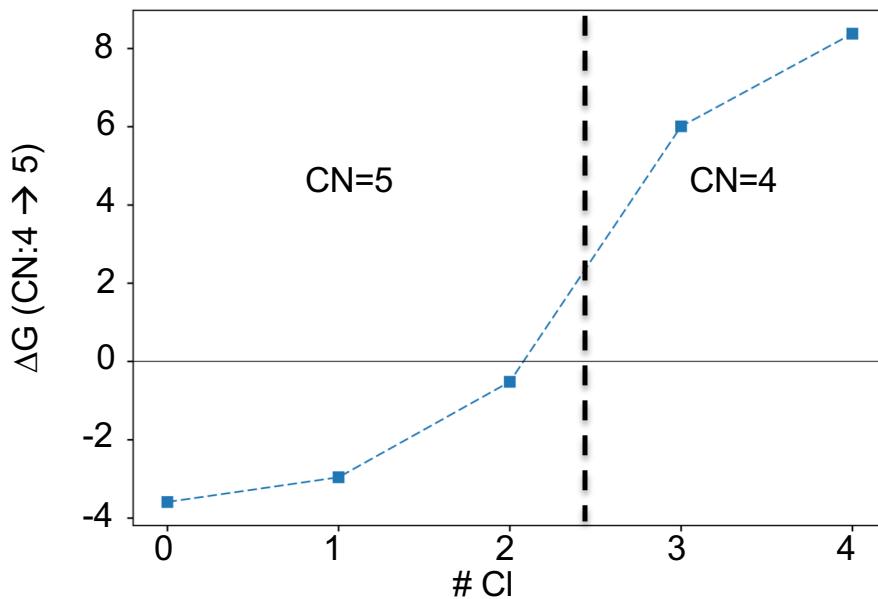
Structures as function of number of chlorine atoms coordinated:



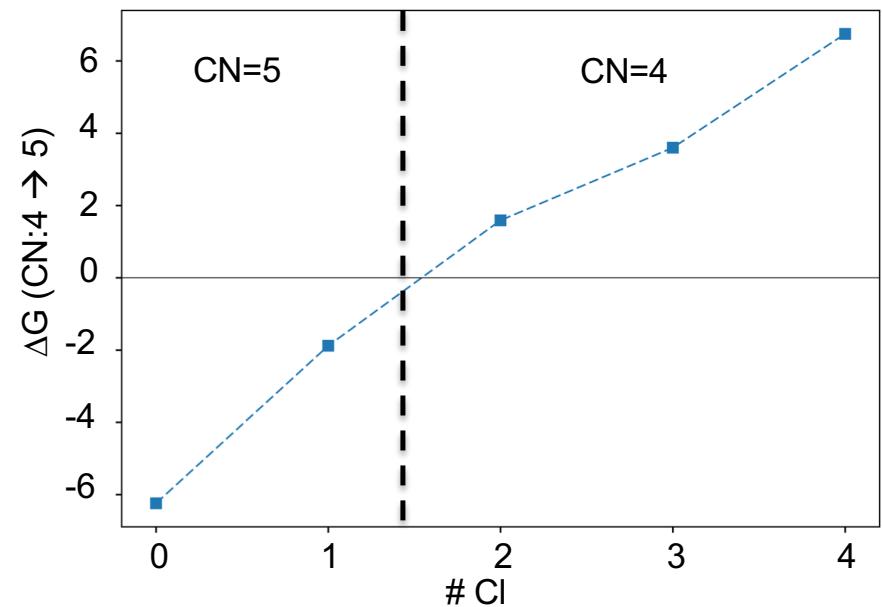
For 4-coordination environment, stable structures identified for 0 to 4 chlorine atoms
 Structures not necessarily thermodynamically stable.

Water Addition Free Energy: UO_2 vs PuO_2

Plutonyl



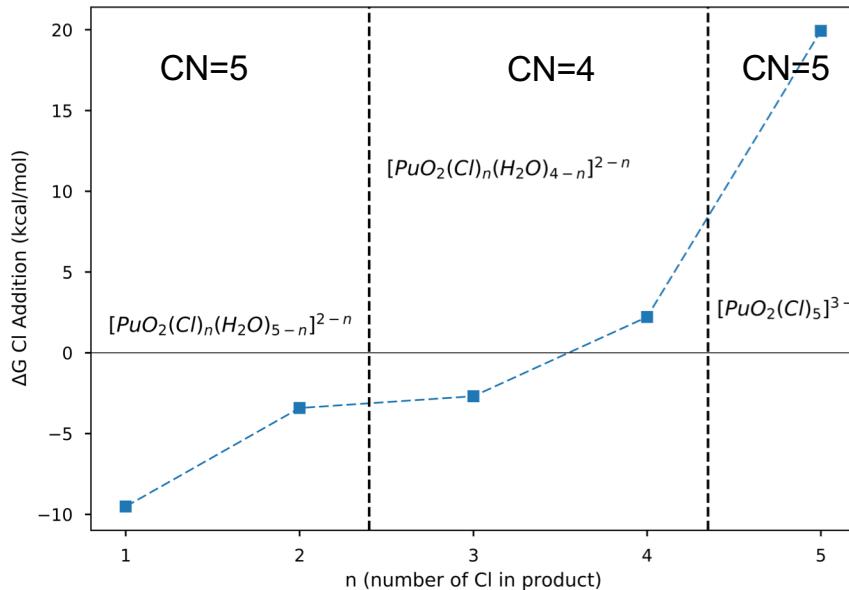
Uranyl



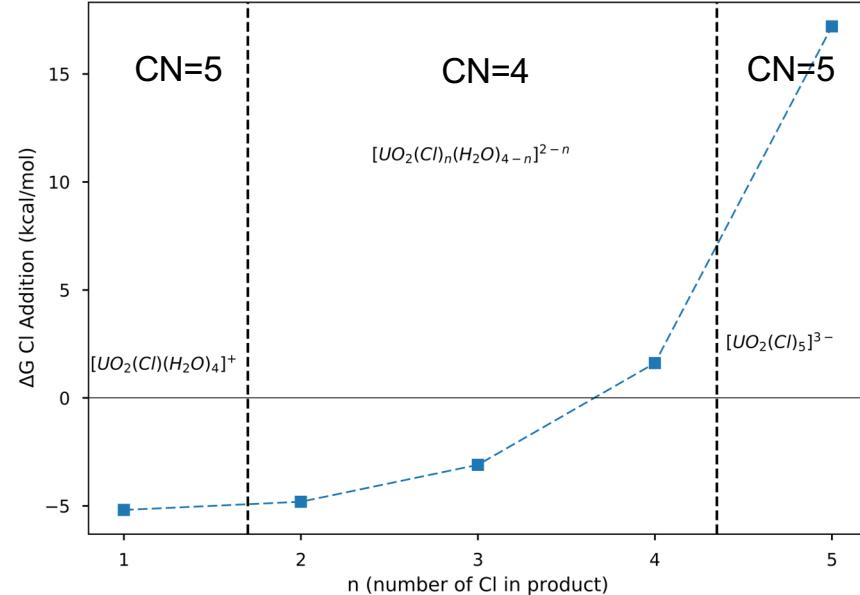
- PuO_2^{2+} CN=5 thermodynamically favorable for up to 2 Cl⁻
- Beyond 2 Cl coordinated we predict the release of a water molecule.

Stepwise Cl Addition

Plutonyl

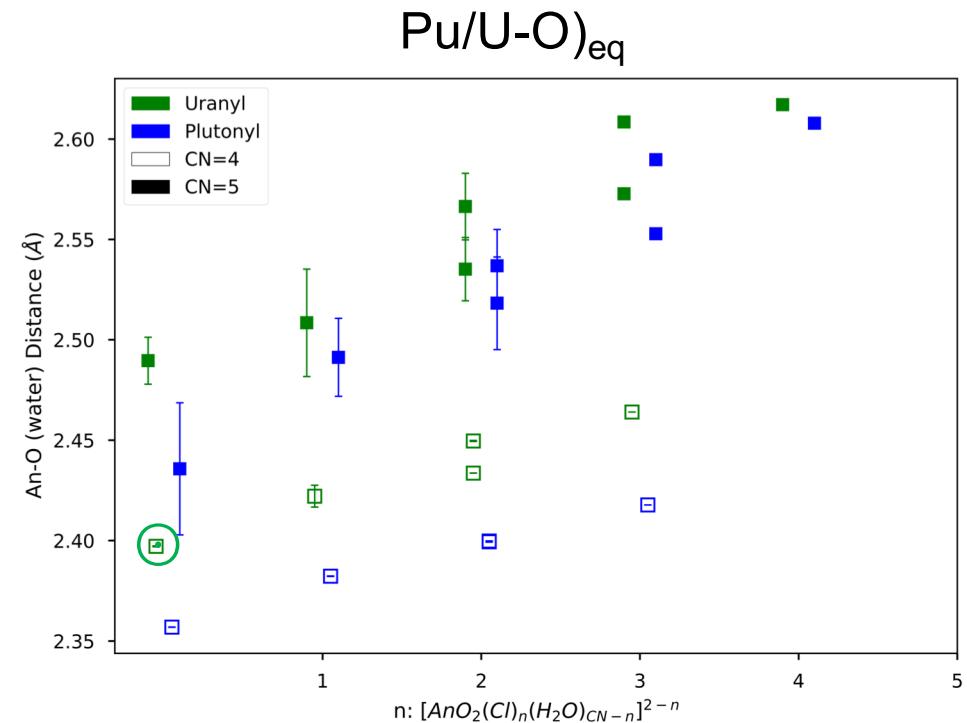
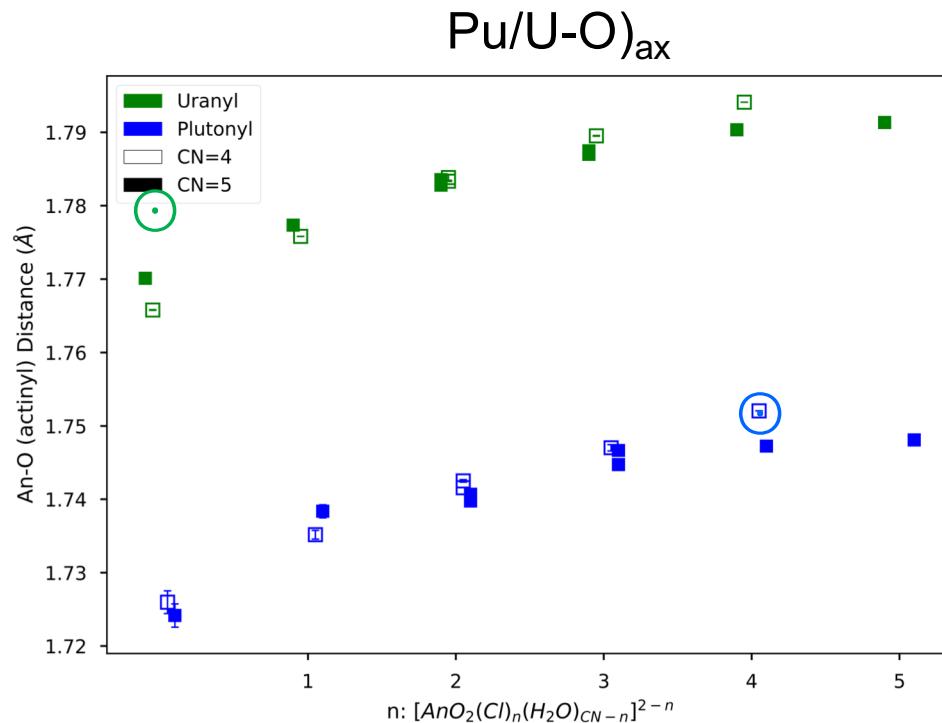


Uranyl



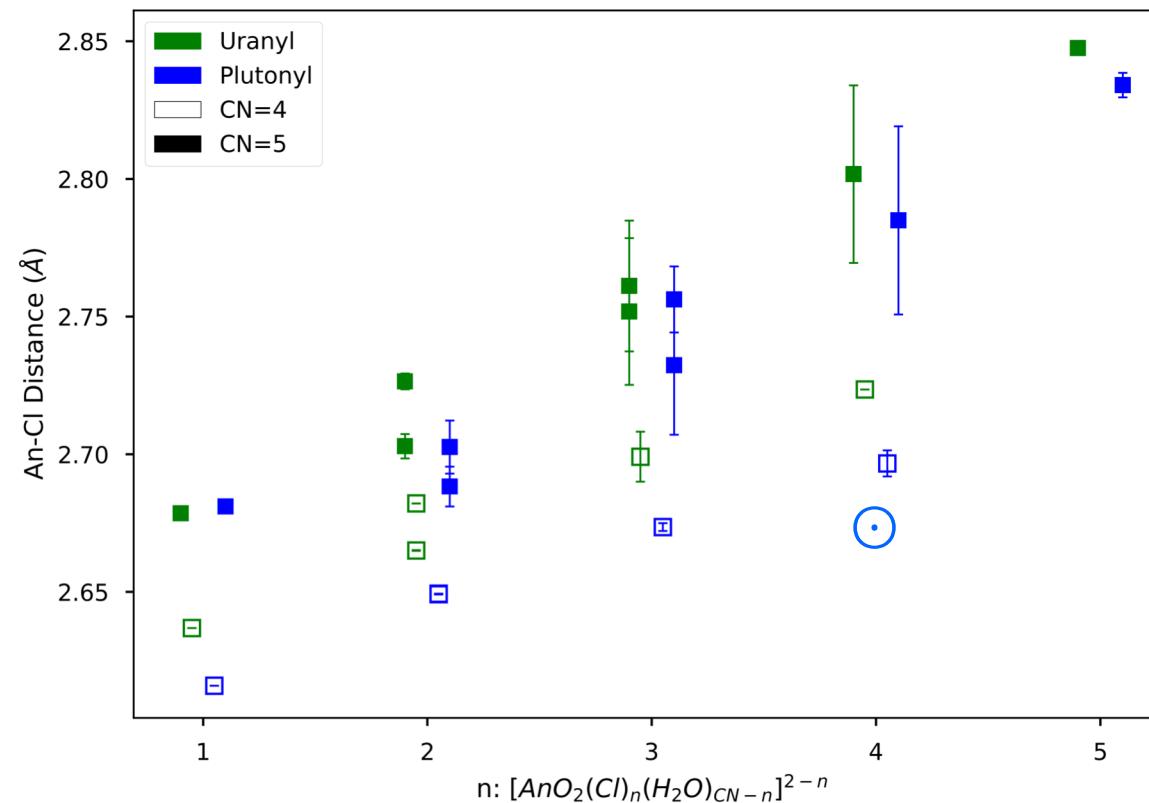
- Both UO_2^{2+} and PuO_2^{2+} predicted to coordinate up to 3 Cl^-
- CN is different for 2 Cl^- coordinated to the actinides;
CN=4 for UO_2^{2+} and CN=5 for PuO_2^{2+}

An-O Distances (actinyl)



As expected from the actinide contraction, $\text{Pu}-\text{O})_{\text{ax}}$ distances systematically shorter than $\text{U}-\text{O})_{\text{ax}}$

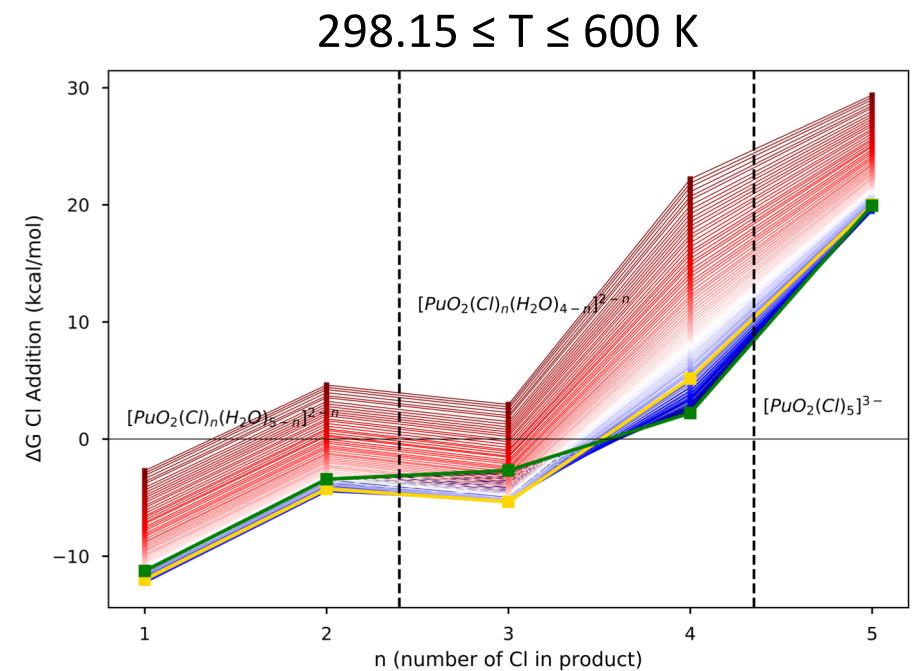
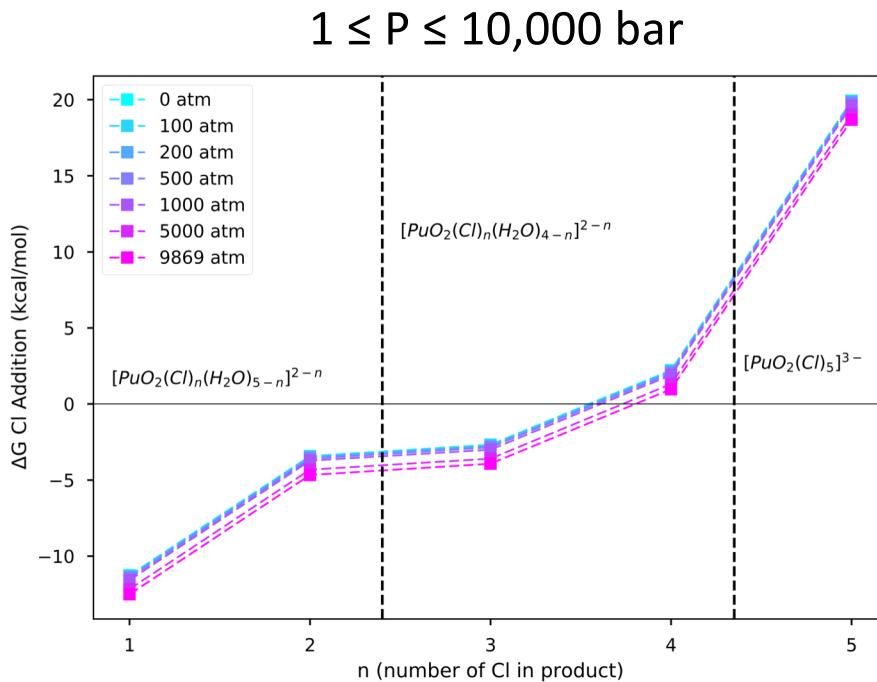
An-Cl Distances



- An-Cl distances increase with increasing Cl count due to repulsion
- Predicted structure for $\text{PuO}_2(\text{Cl})_4^{2-}$ in close agreement to little data available

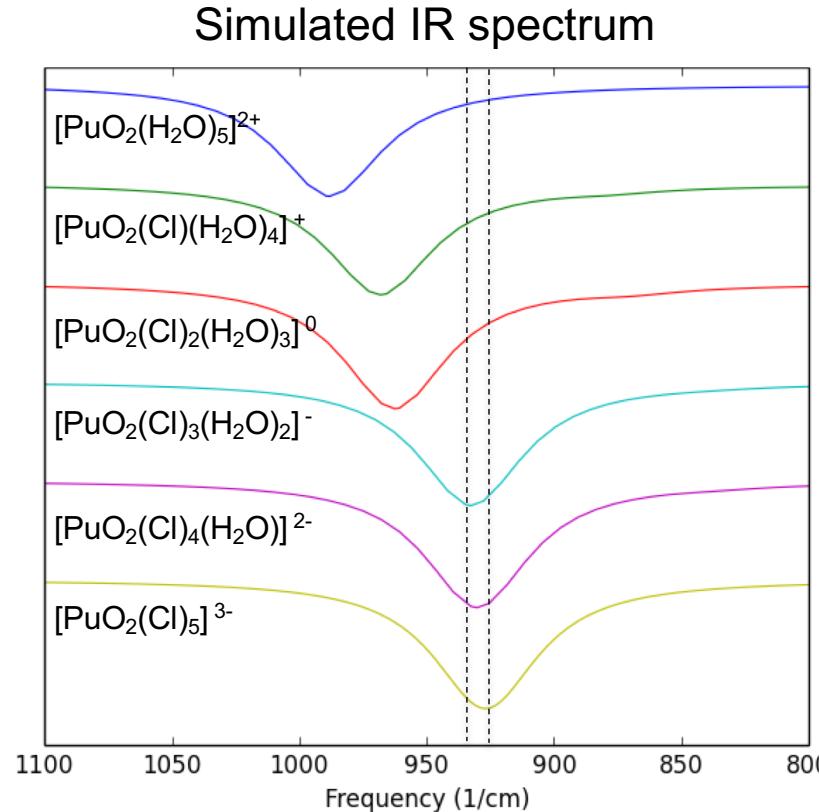
Experimental data for $\text{PuO}_2(\text{Cl}_4)^{2-}$ from: M. Wilkerson and B. Scott Acta Crystallographica Section E (2008)

P/T effects on PuO₂—Cl coordination



- Similarly to UO₂²⁺ the effect of pressure in PuO₂²⁺ is to stabilize the complexes
- Temperature has an opposite effect as pressure, partially cancelling each other

O=Pu=O vibrational frequencies



System	Sym. (cm^{-1})	Asym. (cm^{-1})	$\Delta\nu$
$[\text{PuO}_2(\text{H}_2\text{O})_5]^{2+}$	910	988	78
$[\text{PuO}_2(\text{Cl})(\text{H}_2\text{O})_4]^+$	878	968	90
$[\text{PuO}_2(\text{Cl})_2(\text{H}_2\text{O})_3]^0$	861	950	89
$[\text{PuO}_2(\text{Cl})_3(\text{H}_2\text{O})_2]^-$	841	932	91
$[\text{PuO}_2(\text{Cl})_4(\text{H}_2\text{O})]^{2-}$	837	930	93
$[\text{PuO}_2(\text{Cl})_5]^{3-}$	832	927	95
$[\text{PuO}_2(\text{H}_2\text{O})_4]^{2+}$	916	994	78
$[\text{PuO}_2(\text{Cl})(\text{H}_2\text{O})_3]^+$	881	965	84
$[\text{PuO}_2(\text{Cl})_2(\text{H}_2\text{O})_2]^0$	857	944	87
$[\text{PuO}_2(\text{Cl})_3(\text{H}_2\text{O})]^-$	841	930	89
$[\text{PuO}_2(\text{Cl})_4]^{2-}$	826	918	92

- Computed Symmetric Stretch shift of 36cm^{-1} to higher energy from PuO_2Cl^+ to $\text{PuO}_2\text{Cl}_3^-$ species
- Smaller effect than in UO_2 complexes
- IR versus Raman 90 cm^{-1} apart

PuO₂-Cl summary

- » Predicted species of $\text{PuO}_2(\text{Cl})_n(\text{H}_2\text{O})_{x}^{2-n}$ with $n=0—3$
- » PuO₂ di-chloride expected to be penta-coordinated
- » IR and Raman predictions available for contrasting with upcoming experimental measurements

Future work

- » Submit $\text{UO}_2 + \text{Cl}$ coordination work incorporating experimental data
- » Finalize and write up $\text{PuO}_2 + \text{Cl}$ coordination calculations
- » $\text{NpO}_2 + \text{Cl}$ coordination work: Just started need to finish calculations

Uranyl-Chloride Calculated UV-Vis

